

# FLAME RETARDANT POLYMER NANOCOMPOSITES

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## P2 THROUGH NANOTECHNOLOGY

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# GENERAL FLAME RETARDANT APPROACHES FOR POLYMERS

## I- Gas Phase Flame Retardants

- Reduce Heat of Combustion ( $\Delta H_c$ ) resulting in incomplete combustion.
- Inherent Drawbacks: Negative Public Perception!

## II- Endothermic Flame Retardants

- Function in Gas Phase and Condensed Phase
- Via endothermic release of  $H_2O$ , polymer cooled and gas phase diluted.
- Inherent Drawback: High loadings (30-50%) degrade mechanical properties.

## III- Char Forming Flame Retardants

- Operate in Condensed Phase
- Provides thermal insulation for underlying polymer and a mass transport barrier, preventing or delaying escape of fuel into the gas phase.
- Inherent Drawback: High loadings (20-50%) degrade mechanical properties.

**Goal: develop cost effective, environmentally friendly approaches to reduce flammability and improve physical properties**

# Polymer clay Nanocomposite

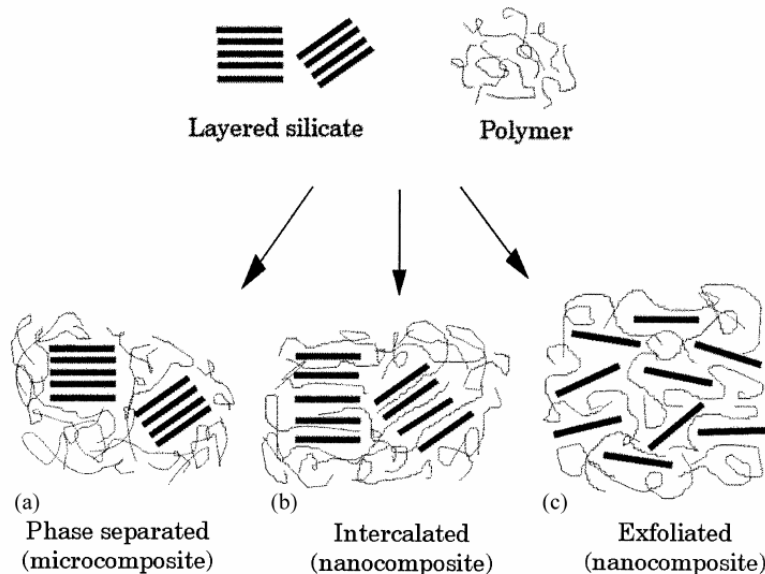
## Materials:

Layered silicates, organic modifier, polymer matrix

## Processing Techniques:

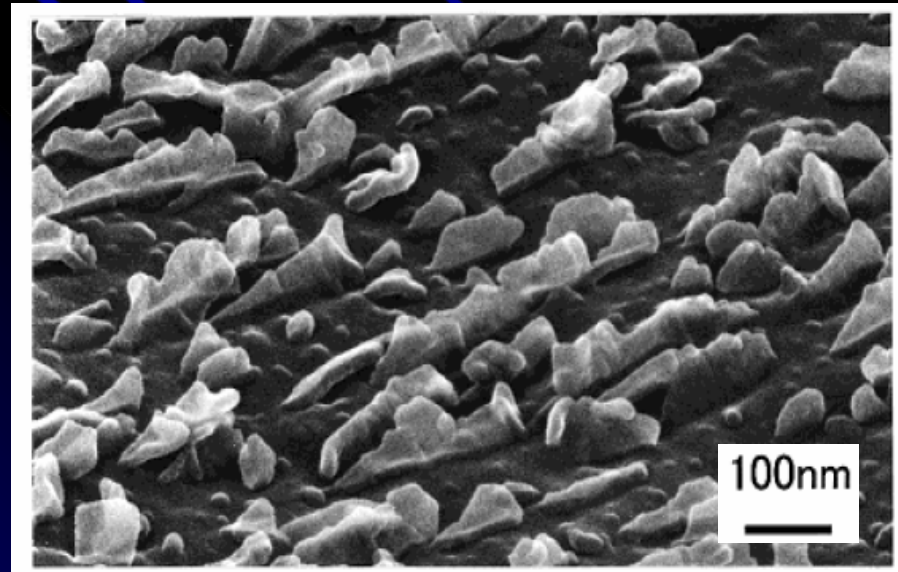
- Solution mixing and film casting
- Melt mixing (extrusion, injection molding)
- In situ polymerization

## Morphologies (Simplified picture):

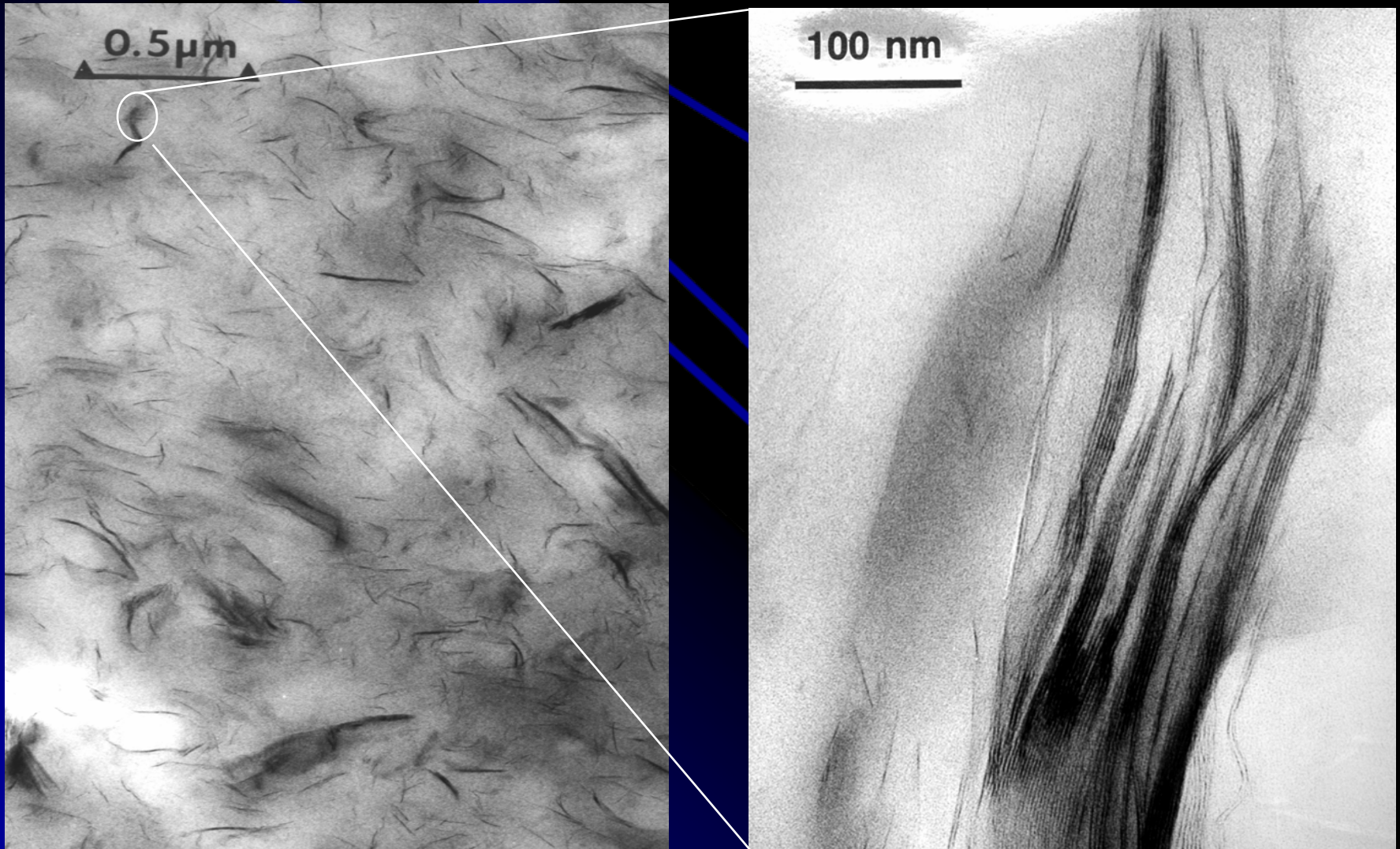


## Properties:

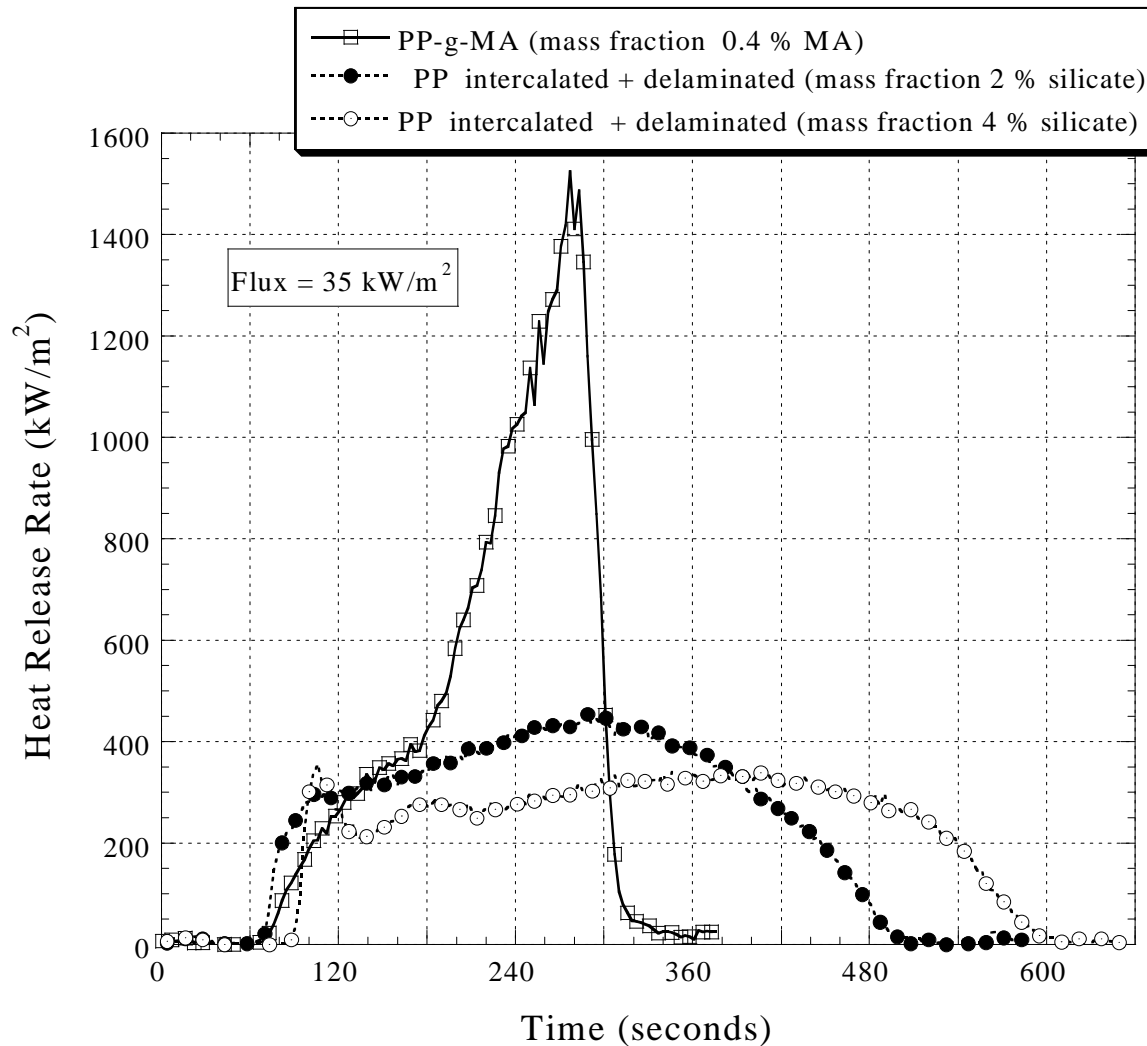
- Flame resistance
- Improved gas permeability
- Higher stiffness
- Scratch resistance
- Higher glass transition
- Improved thermo-mechanical response



# PP-clay Nanocomposite: TEM

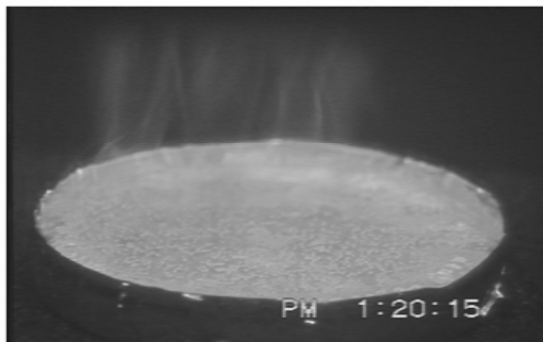


# PP-clay Nanocomposite: Cone Calorimetry



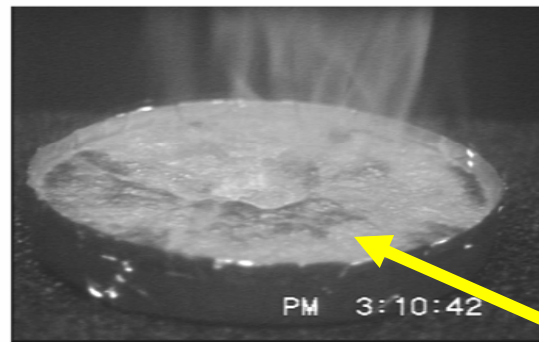
# Gasification of Polystyrene Layered-silicate Nanocomposites

PS (100%)

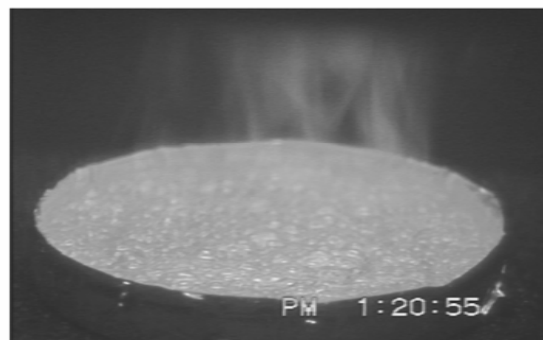


50 s

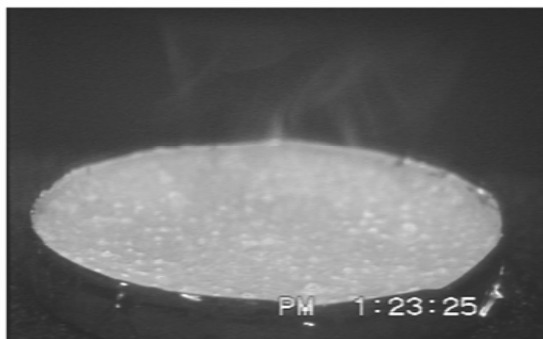
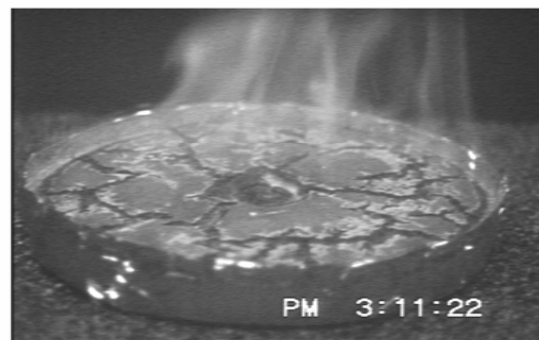
PS (95%) + MMT (5%)



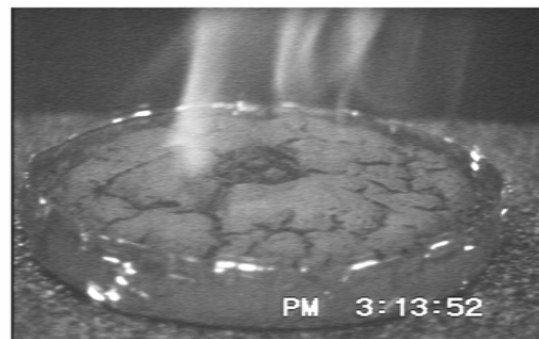
Char  
or  
Coke  
Formation



90 s

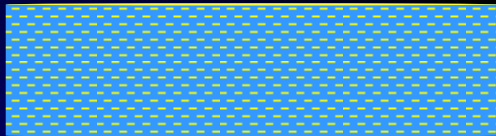


240 s



# CRITICAL CRITERIA FOR FORMATION OF HOMOGENEOUS CHAR

Homogeneous clay  
dispersion in polymer



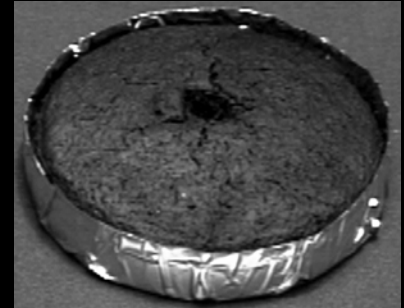
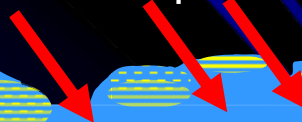
homogeneous char:  
thermal barrier



Pyrolysis and phase separation



discontinuous char:  
Poor thermal protection



Unstable and inhomogeneous  
clay dispersion in polymer

Depends on: clay loading, dispersion, polymer Mw,  
viscosity, degradation mechanisms,  
carbonaceous char formation

Kashiwagi et al., Polymer, 2004

# NANOCOMPOSITE + CONVENTIONAL FLAME RETARDANT APPROACH

- Nanocomposites + additional flame retardants have resulted in final materials that pass regulatory tests and have superior balances of properties.
  - Successful commercial approaches remove some of existing FR package, replace with nanocomposite.
    - Dupont 1980s –PBT + OMMt + Organo Br- UL94 V0
    - Showa Denko – PBT SynMica + MealmineCY- UL94V0
    - Kabelwerk Eupen: EVA + Organomontmorillonite +  $\text{Al}(\text{OH})_3$ . – UL1666
    - PolyOne: (polyolefin nanocomposite – UL-94 V-0 @ 3.0mm)
    - Strathclyde –PU Foam + OMMt + FR – pass crib-5
    - Nanocor – Phos. Clay - UL94 V0
    - U mass Lowell – Clay- ELO as substitute for Pb in PVC

# Challenges

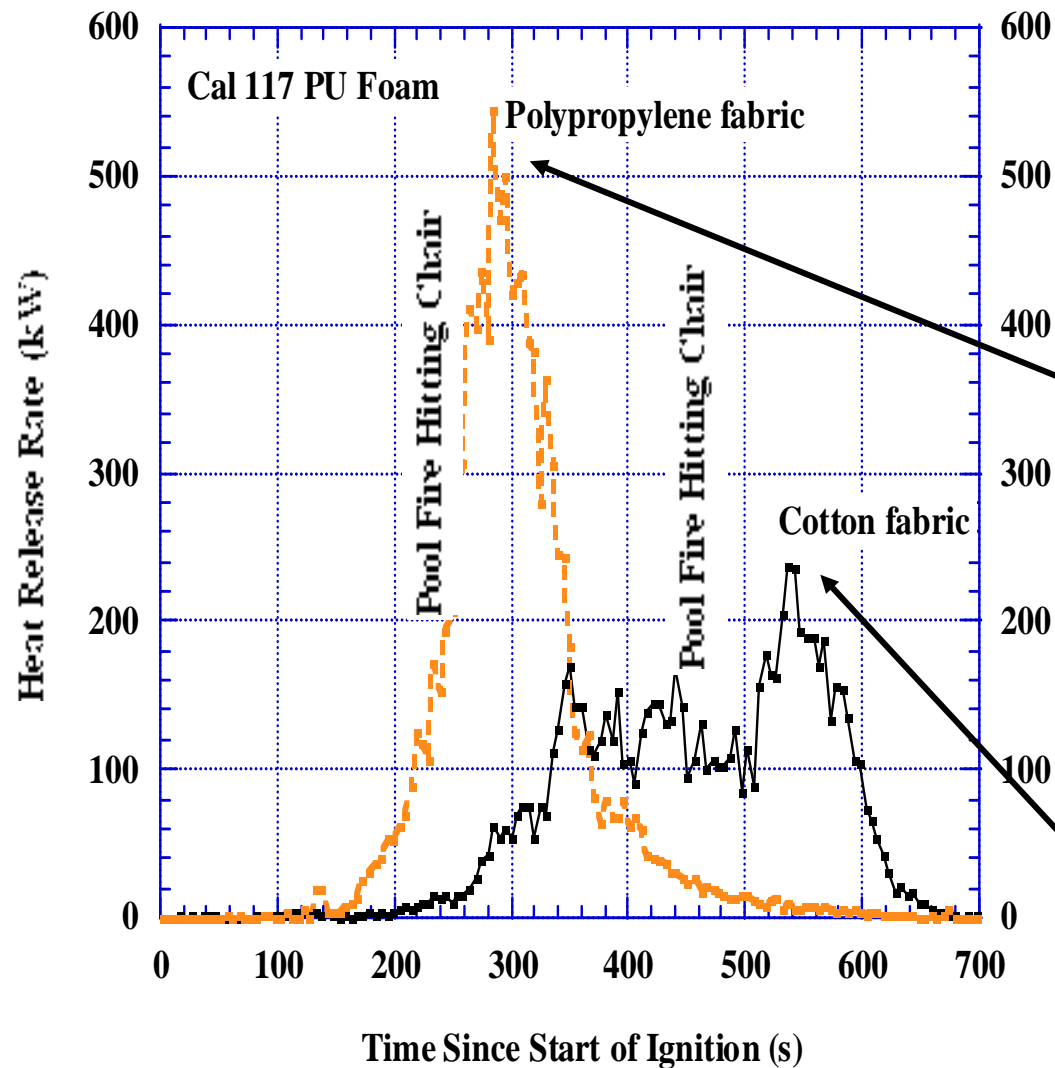
1) Furniture and mattress fires still cause  
~1000 deaths/yr and cost \$ 500 M/yr

1) **Objective:** to evaluate the effectiveness of nanoadditive based flame retardants in reducing the flammability of flexible foams.

2) **Objective :** To improve the ability of barrier fabrics to prevent flame spread in mattresses and furniture using nanoadditives.

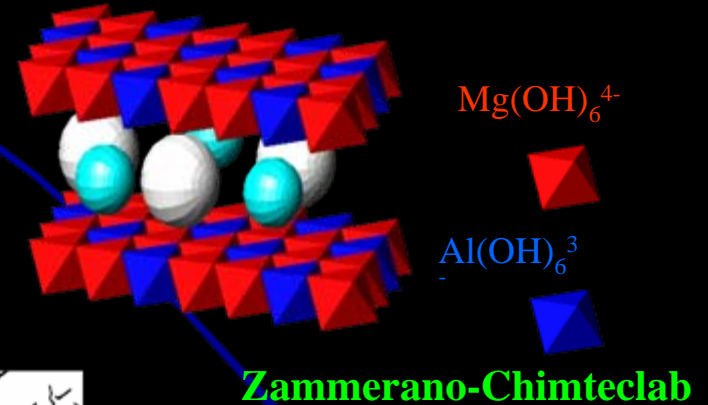


# MELT POOL FIRES DURING FOAM BURNING

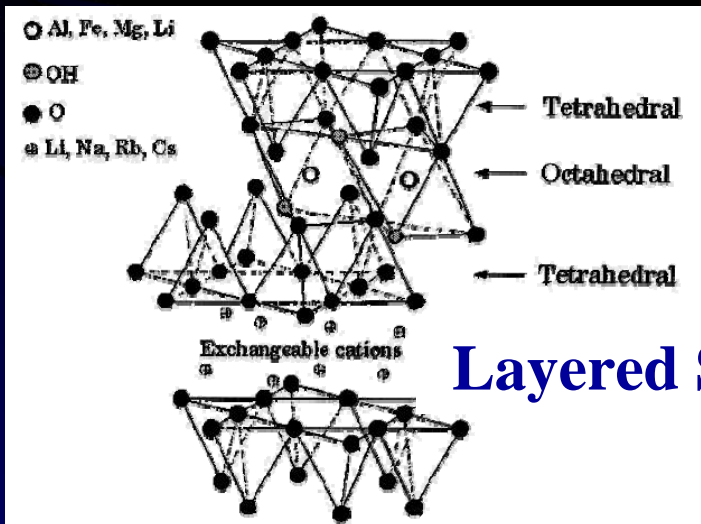


# NANO-ADDITIVES

## Layered Double Hydroxide



## Layered Silicates



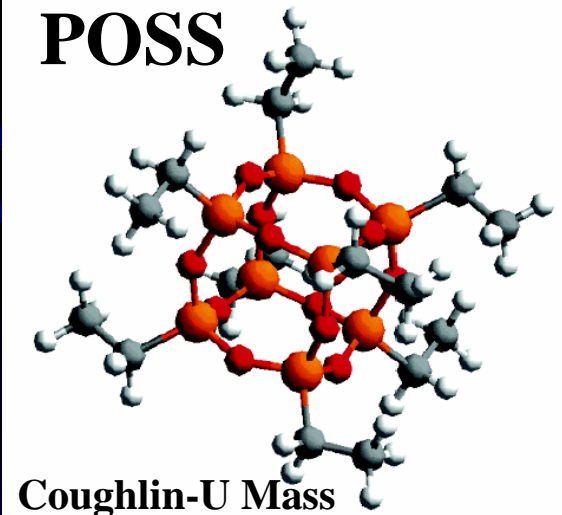
## Nano silica

Kashiwagi - NIST

## Carbon nanotubes

Bellayer - NIST

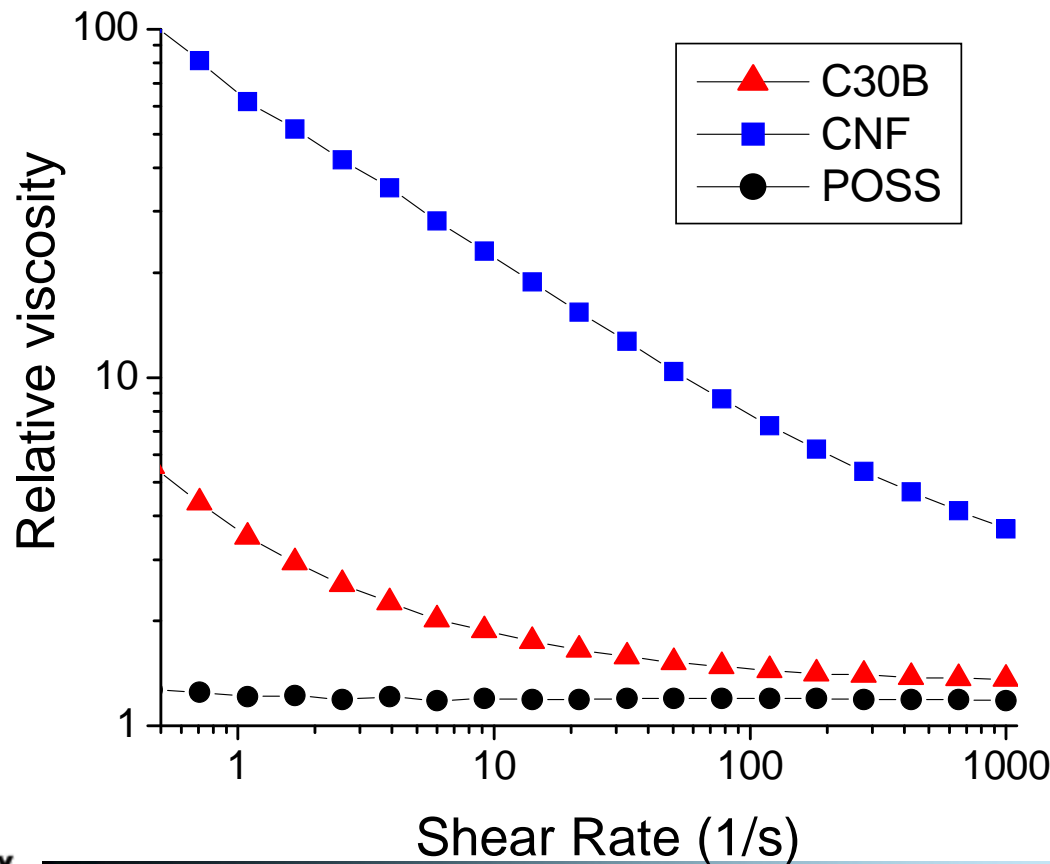
## POSS



# Flame Retardant Mechanism

High aspect ratio nanoadditives (e.g. CNF) properly dispersed in the polymeric matrix form a percolated jammed structure, due to particle-particle interactions, so that the melt behaves rheologically like a gel

- **Inhibition of dripping**



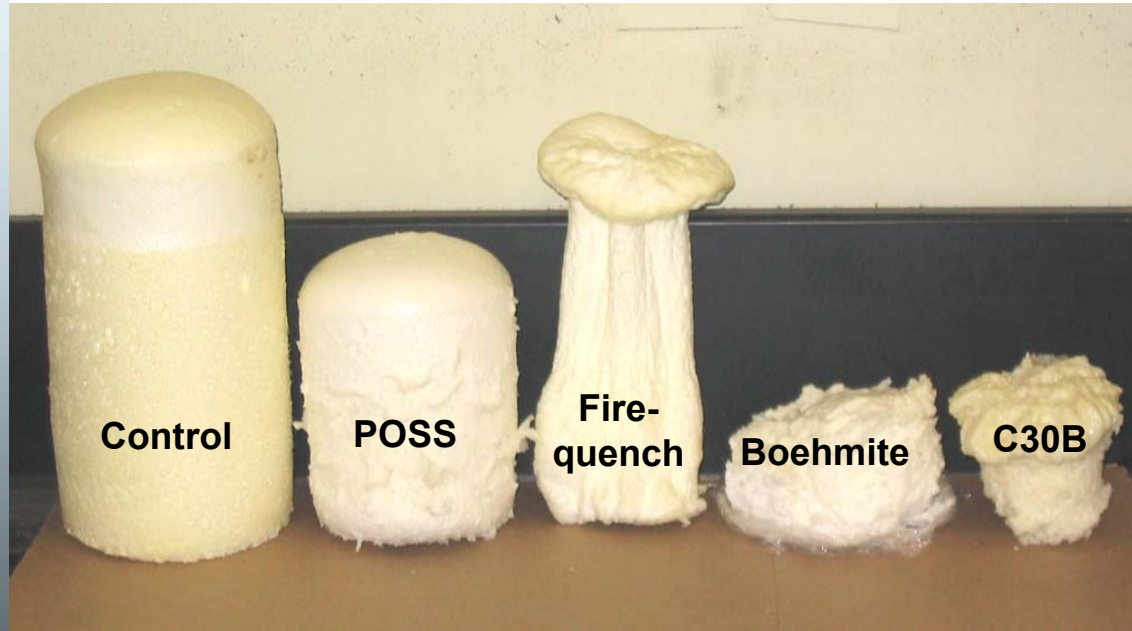
# Modified/Nano Formulations

6.6 parts of Br-P FR in the standard formulation are replaced by 6.6 parts inorganic additive (e.g., CNF, Na<sup>+</sup> MMT, LDH and Boehmite)

When organo-modified additive are used (e.g., OMMT) the amount of additive is increased in order to keep constant the inorganic fraction of the additive.

	Br-P FR (wt.%)	Nano-additive (wt.%)
Br-P FR (Control 1)	6.2	0
Talc (Control 2)	2.3	3.9
CNF	2.3	3.9
Boehmite	2.3	3.9
LDH	2.3	3.9
OMMT (C30B)	2.3	5.1
POSS	2.3	5.1

# Foam Processing Optimization

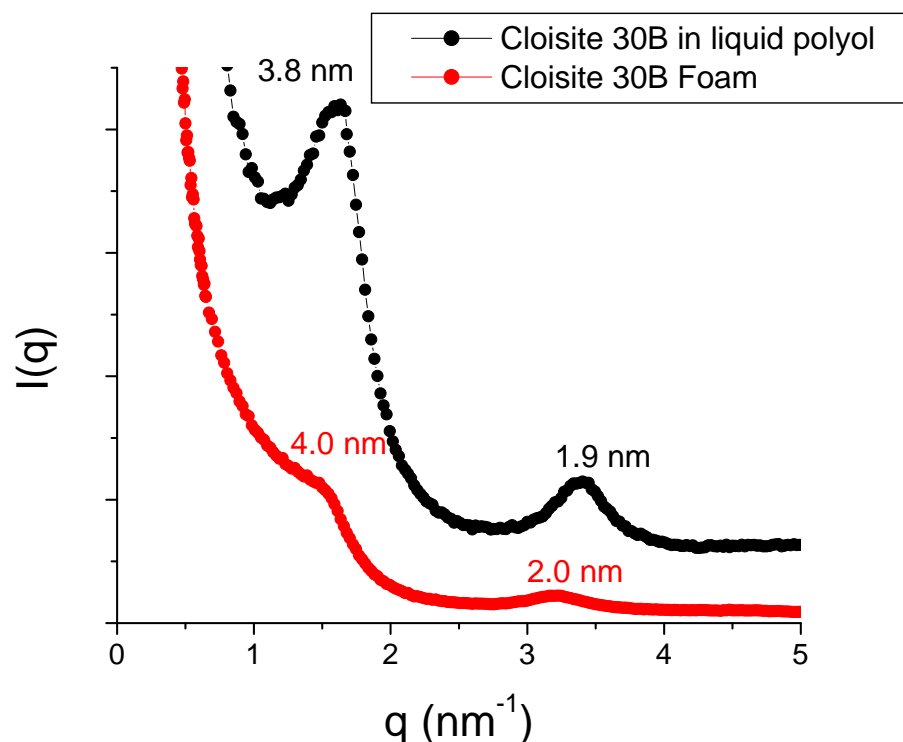


**Non-optimized foam samples with various additives.**

**Each formulation needs to be individually tuned to match the control formulation.**

1. Adjustment of the polyol – nanoparticle dispersion viscosity by coupling agents.
2. Optimization of the curing and blowing reaction through suitable catalysis ratios.
3. Prevention of collapse and shrinkage by appropriate surfactants and cell openers.
4. Monitoring of the foam rise and curing with a FOAMAT foam qualification system.
5. Evaluation of the foam quality by optical analysis, density and air flow measurements.

# Characterization of Nanoparticles Dispersions

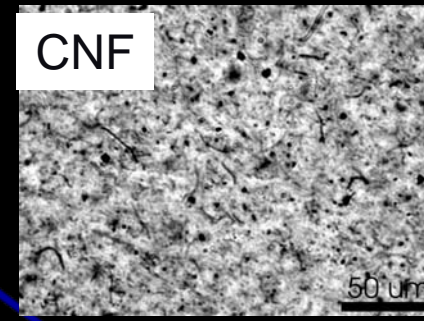
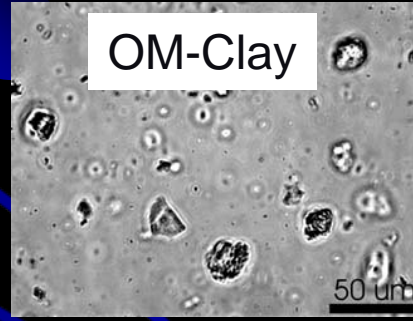
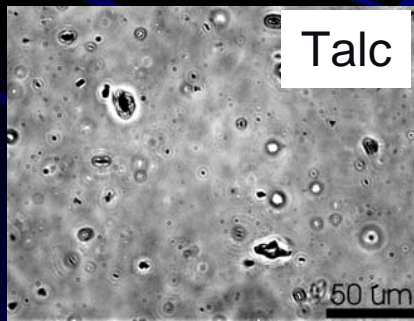


Small Angle X-Ray Scattering

	Median Size ( $\mu\text{m}$ )
Cloisite 30B	100
Boehmite	0.2
POSS	8
CNF	-

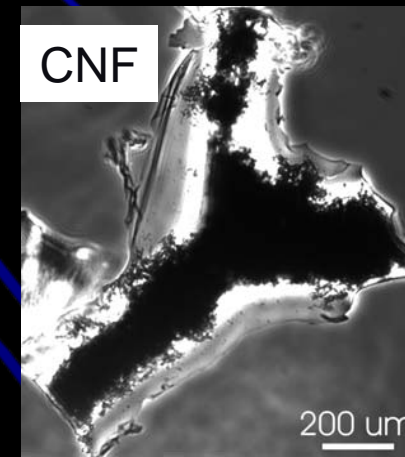
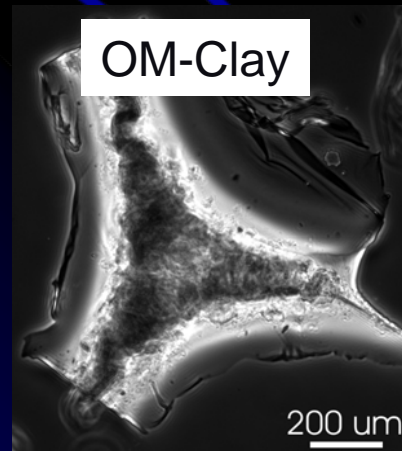
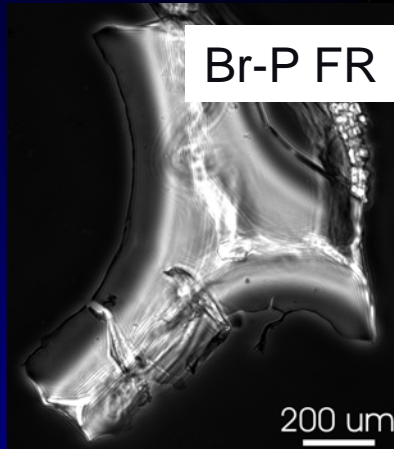
Aggregate size estimation by means of Static Laser Scattering

# FOAM CHARACTERIZATION



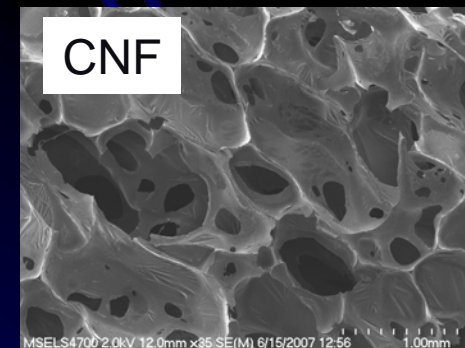
POLYOL

OPTICAL MICROSCOPY



FOAM

SEM



# Modified Cone Calorimetry

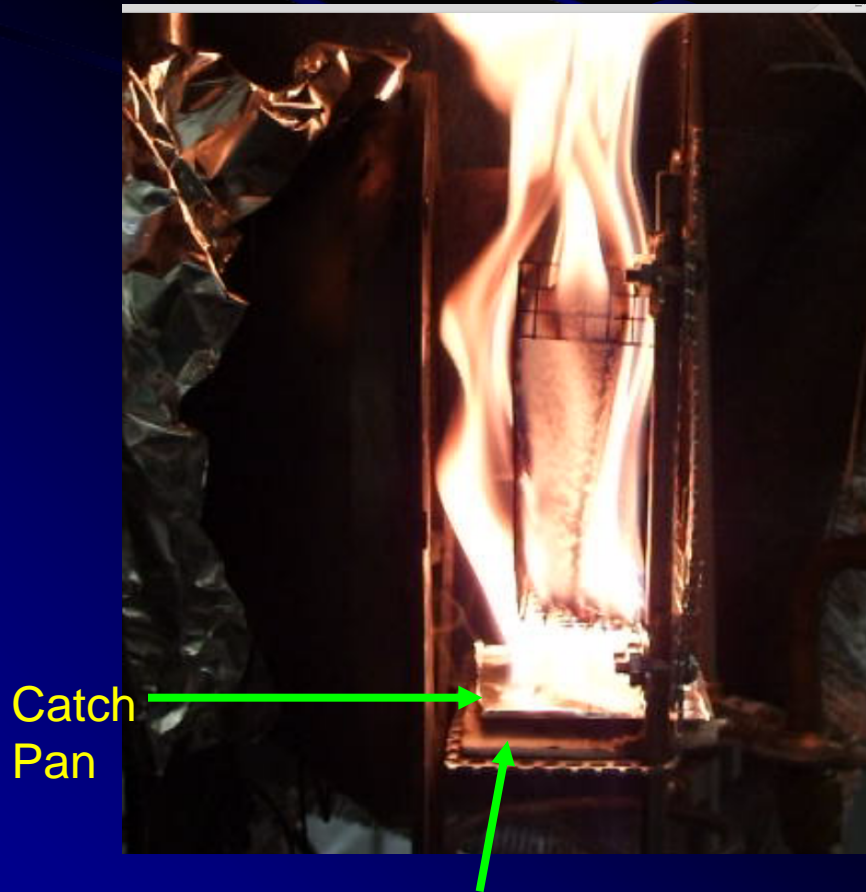


CNF Foam



Cloisite 30B Foam

# NANOADDITIVE FLAME RETARDANTS FOR POLYURETHANE FOAM



**Pool-fire**

**PU FR-foam control**



**no Pool-fire**

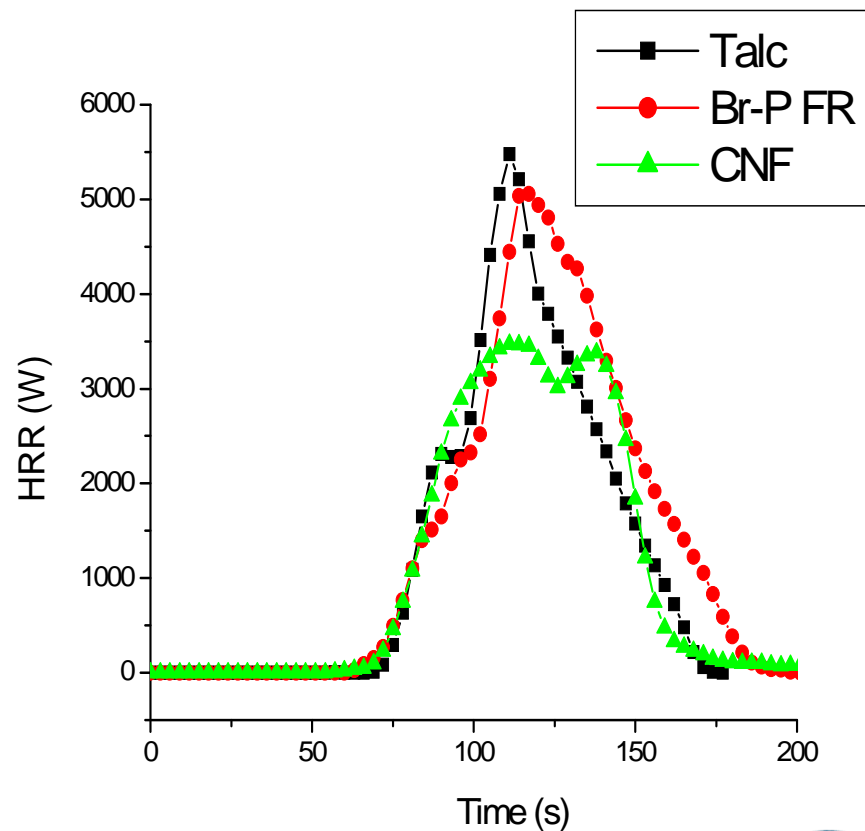
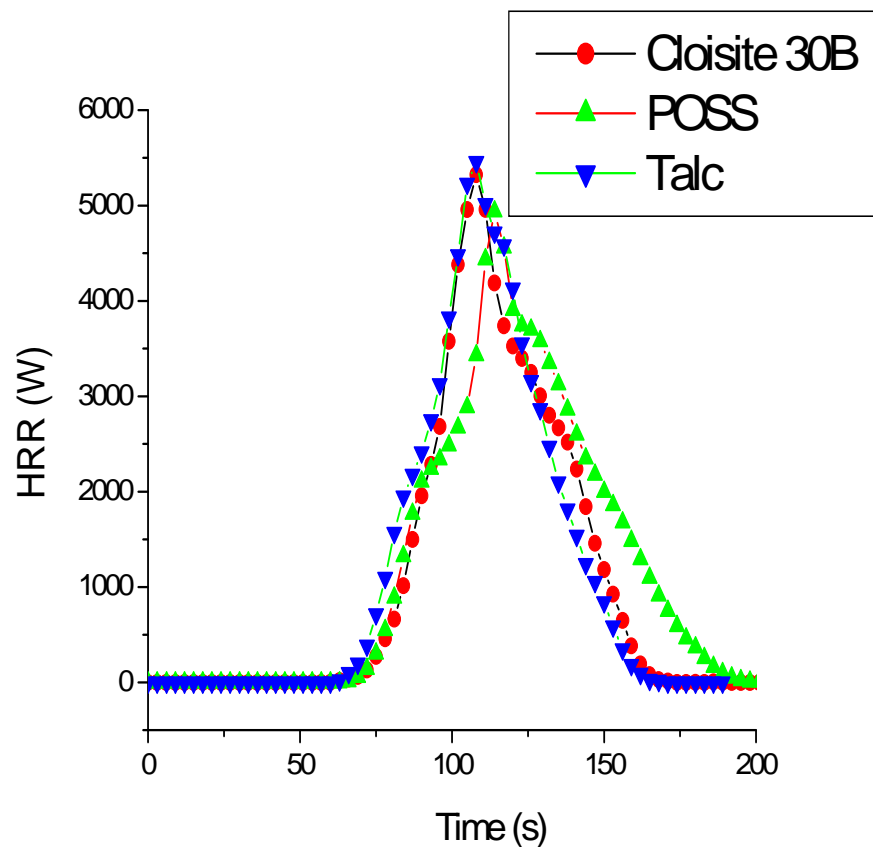
**PU FR-foam + 4% Carbon Nano-Fibers:**

Tom Ohlemiller, Richard Harris, J. Randy Shields,  
Mauro Zammarano (GR), Roland Krämer (GR)

Viscosity  
Nano-Graphite

# HRR by Modified Cone Calorimetry

External Heat Flux: 11 kW/m<sup>2</sup>



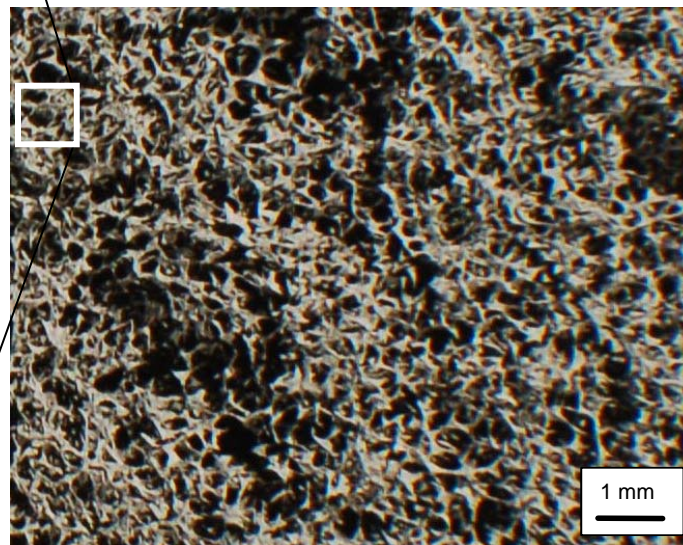
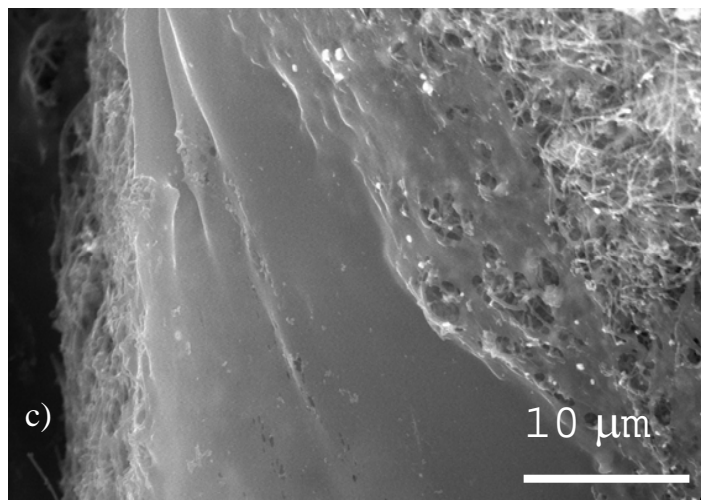
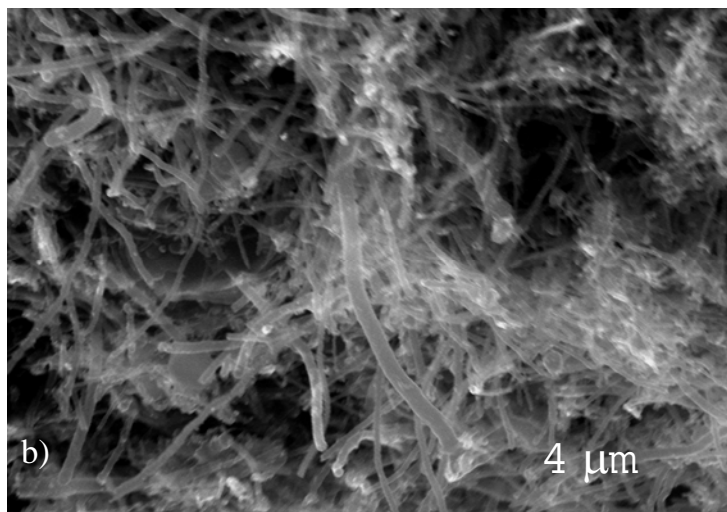
35% reduction in PHRR with CNF

# Flame Retardant Mechanism of CNF

High aspect ratio nanoadditives (*e.g.* CNF) properly dispersed in the polymeric matrix form a percolated jammed structure, due to particle-particle interactions, so that the melt behaves rheologically like a gel\*.

- **Inhibition of dripping**
- **Heat shield effects of network structured protective layer**

# CNF Foam Residue - SEM



Residue of CNF foam after Cone



**P2 THROUGH**  
NANOTECHNOLOGY  
SEPTEMBER 25-26, 2007



## **Environmentally Friendly, Nano-based Polyurethane Fire Retardant Systems**

Professor Richard A. Pethrick,

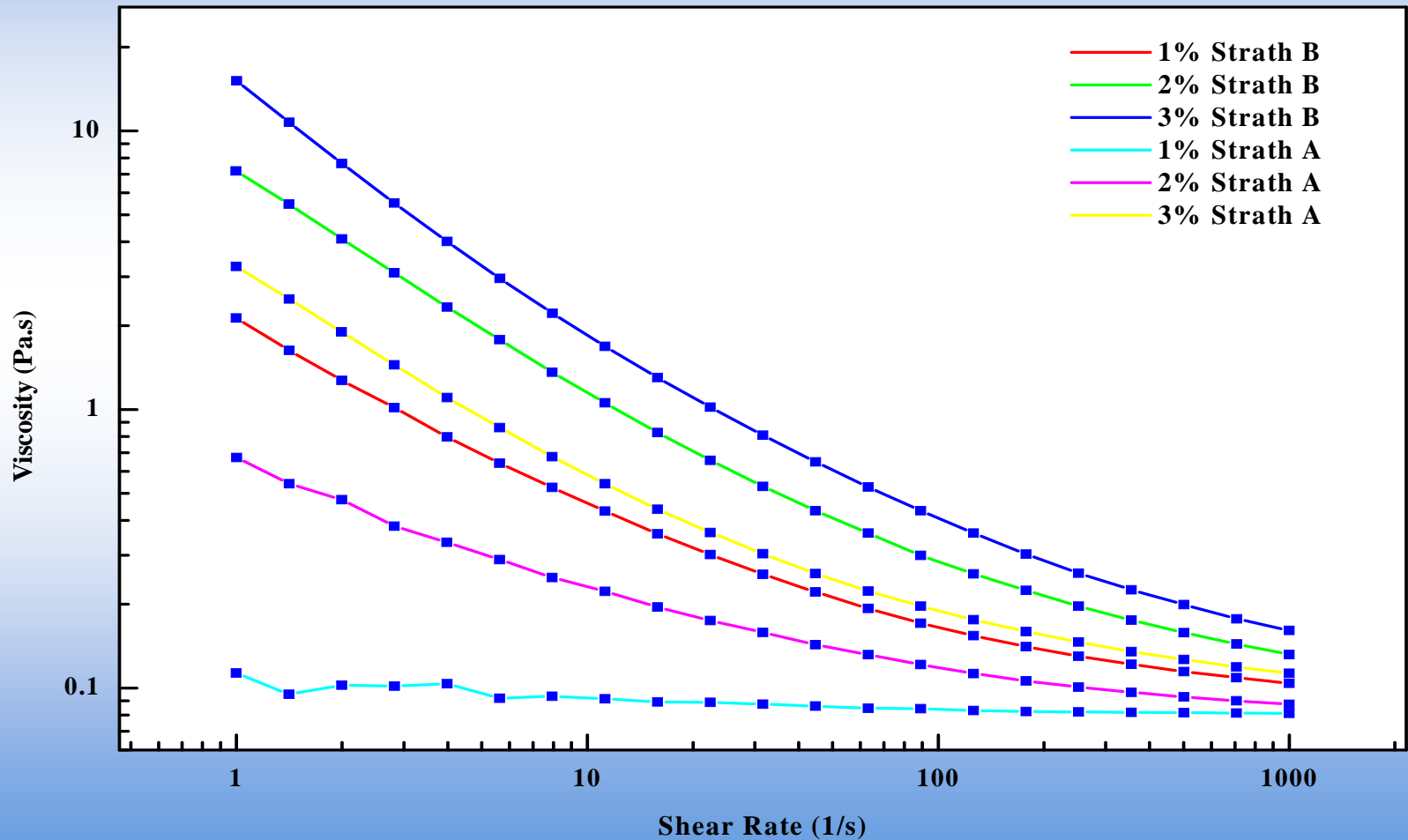
*Department of Pure and Applied Chemistry,  
University of Strathclyde, Thomas Graham  
Building, 295 Cathedral Street Glasgow G1 1XL.*

"Pollution Prevention through Nanotechnology"  
September 25-26, 2007, in Arlington , VA

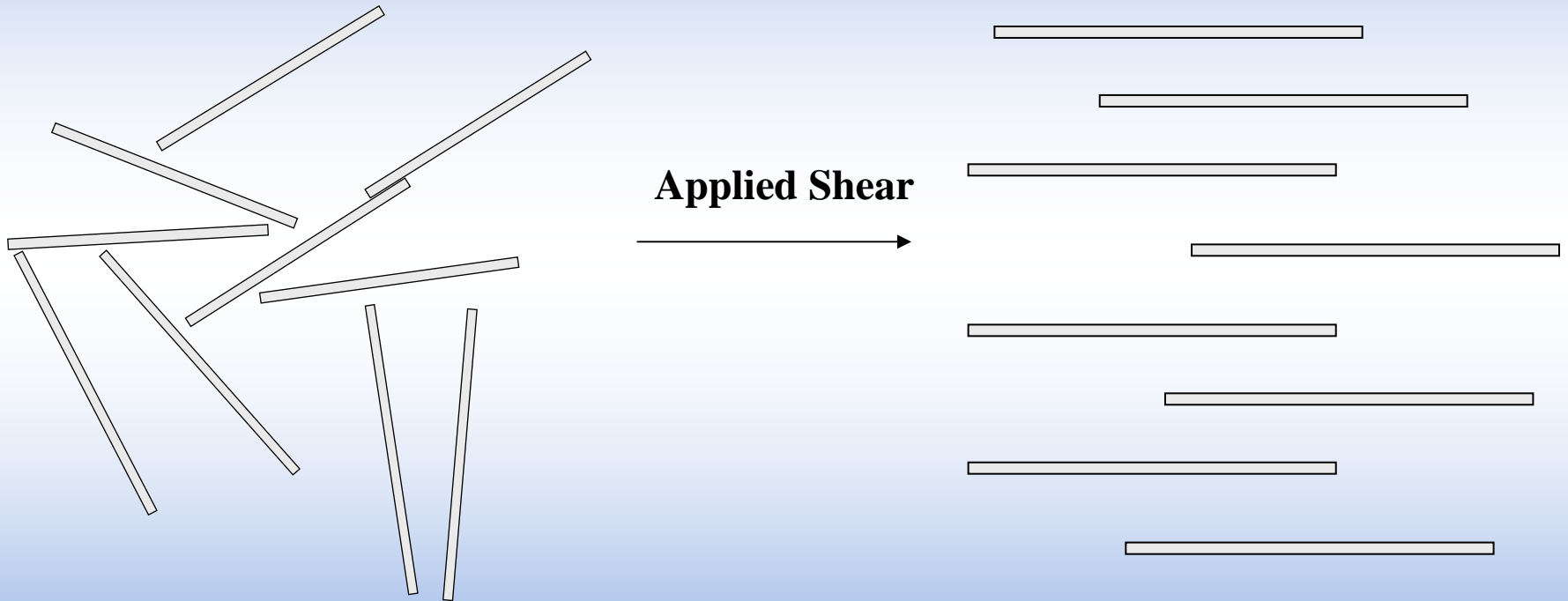


# Effect of dispersion methods -study of PU monomers

Shear thinning of sonicated glycol blends of Strath A / Strath B



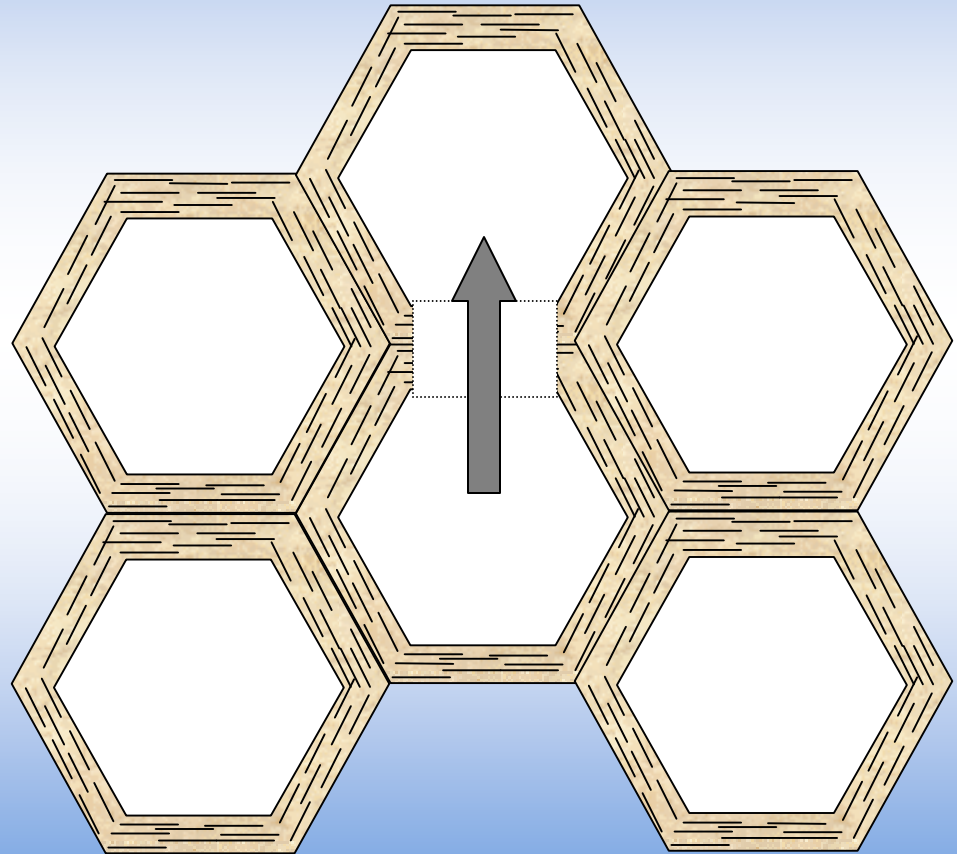
# Alignment of Platelets Due to Shear



**Alignment of the platelets in the shear field leads to a lowering of the viscosity.**

# Flame Retardancy in Polymer Foams.

Nano platlets composite structures within cell walls to inhibit volatile diffusion and enhance the viscoelasticity of the melt phase .



# Flexible Foam Systems

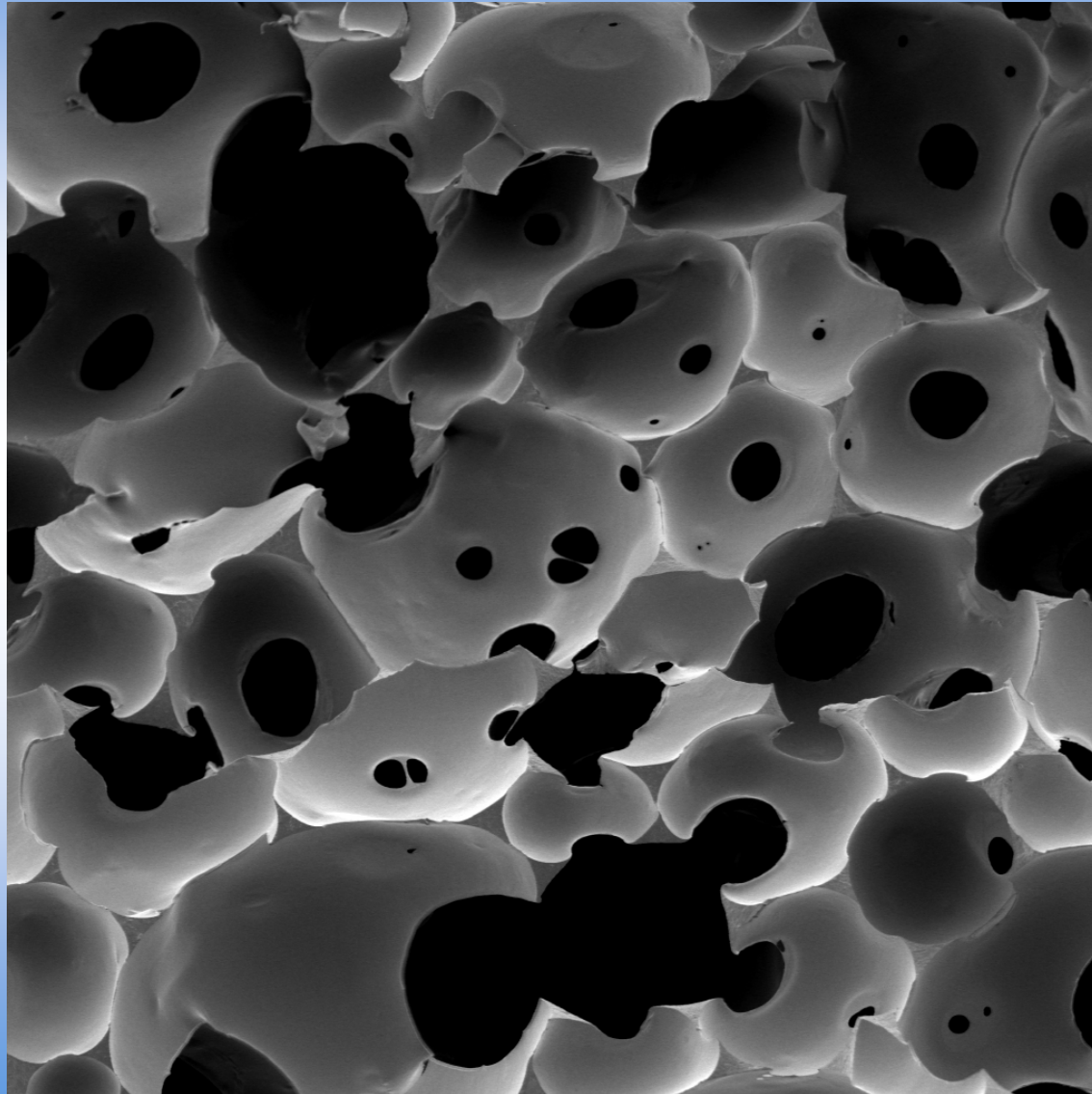
- A series of flexible foam systems have been produced with the required flexibility and incorporating nanocomposite organically modified clay materials.  
{ Patents have been applied for these systems }



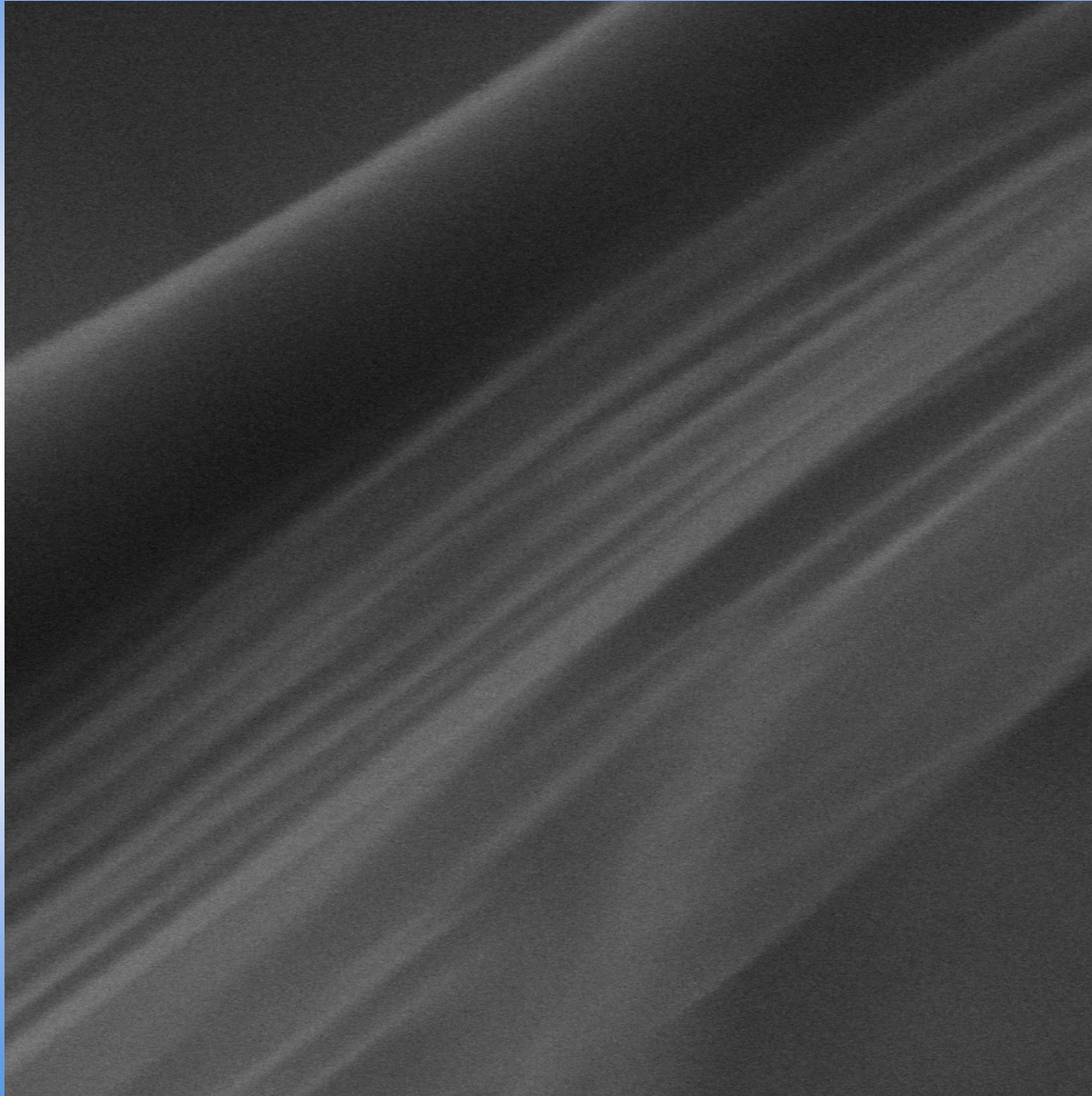
# What do the materials look like?

- Electron microscopy has been performed and they show the nano material is present in the foam walls and has effected the rheology in the foam formation
- The materials have comparable mechanical properties to current flexible foam formulations

# Electron Micrograph of PU foam



# Electron Micrograph of PU Foam Structure



## Crib 5 Testing

### The Challenge:

To  
avoid  
this

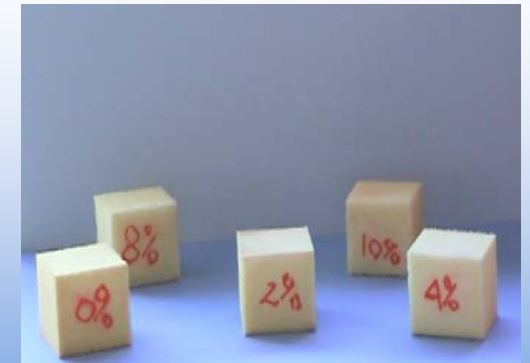


Escalating

Self-extinguishing

Obtain  
this

From these



The Process:  
Formulation design

# Nano Composites

I hope this short presentation has shown that by recognising the natural nano dimensions which exist in **natural** materials it is possible to enhance the properties of conventional materials which we produce and achieve a greater use of these materials.

Nano composites are not all about new exotic materials but can be about using traditional materials more effectively.

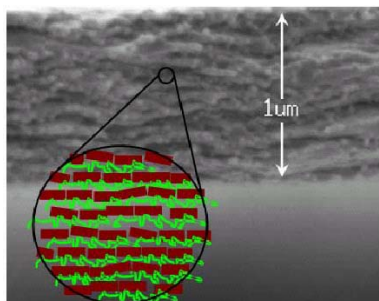
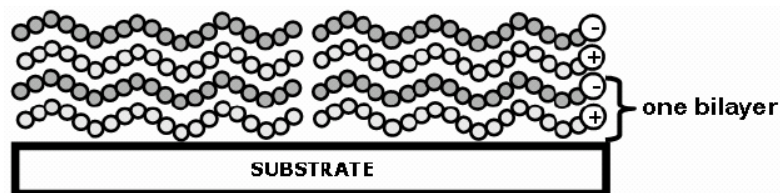
# Acknowledgements

- Dr J.J. Liggat, Dr John Daly,
- Dr Ian Rhoney, Dr Sharon Ingram,
- EPSRC.
- Scottish Enterprise.
- Southern Clay.



# Layer by layer assembly of nanoparticles

Deposition of nanoparticles using layer by layer assembly technique.



**Collaborator: Jaime  
Grunlan, Texas A&M  
University**



**Movie Speed: 10x**

Coated Control Foam:  
2 wt. % coating

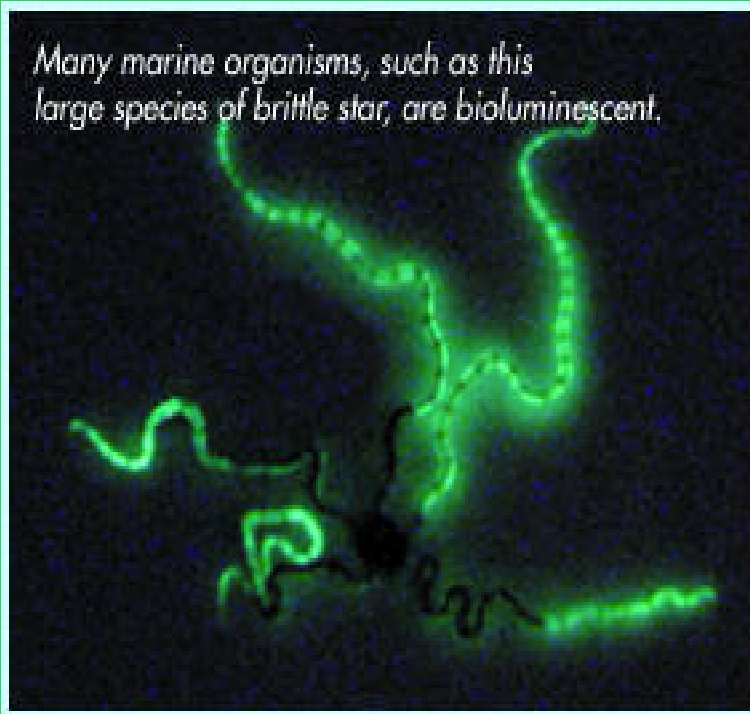
**NIST**

National Institute of  
Standards and Technology



# Methodologies to Determine Health and Environmental effects of Nano-particles

## *Amphipholis squamata*



- Common echinoderm
- Diet consists of particles
- Bioluminescence under nervous control, and produced only under stimulation
- Commonly used in the Deheyn lab to assess sub-lethal effect

Dimitri D. Deheyn, Ph.D.  
Marine Biology Research Division,  
Scripps Institution of Oceanography, University of  
California, San Diego

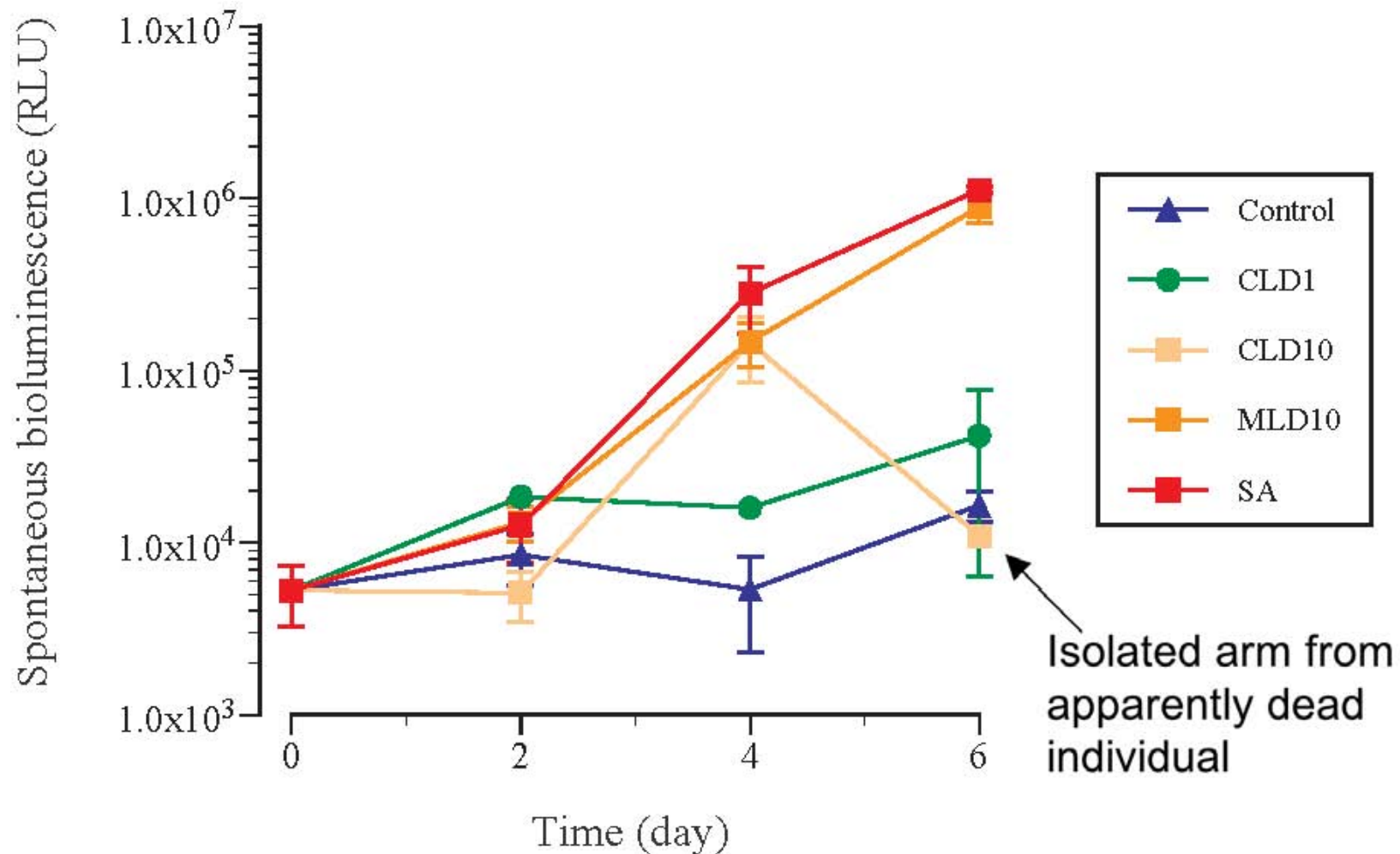
# Experimental setup in aquariums



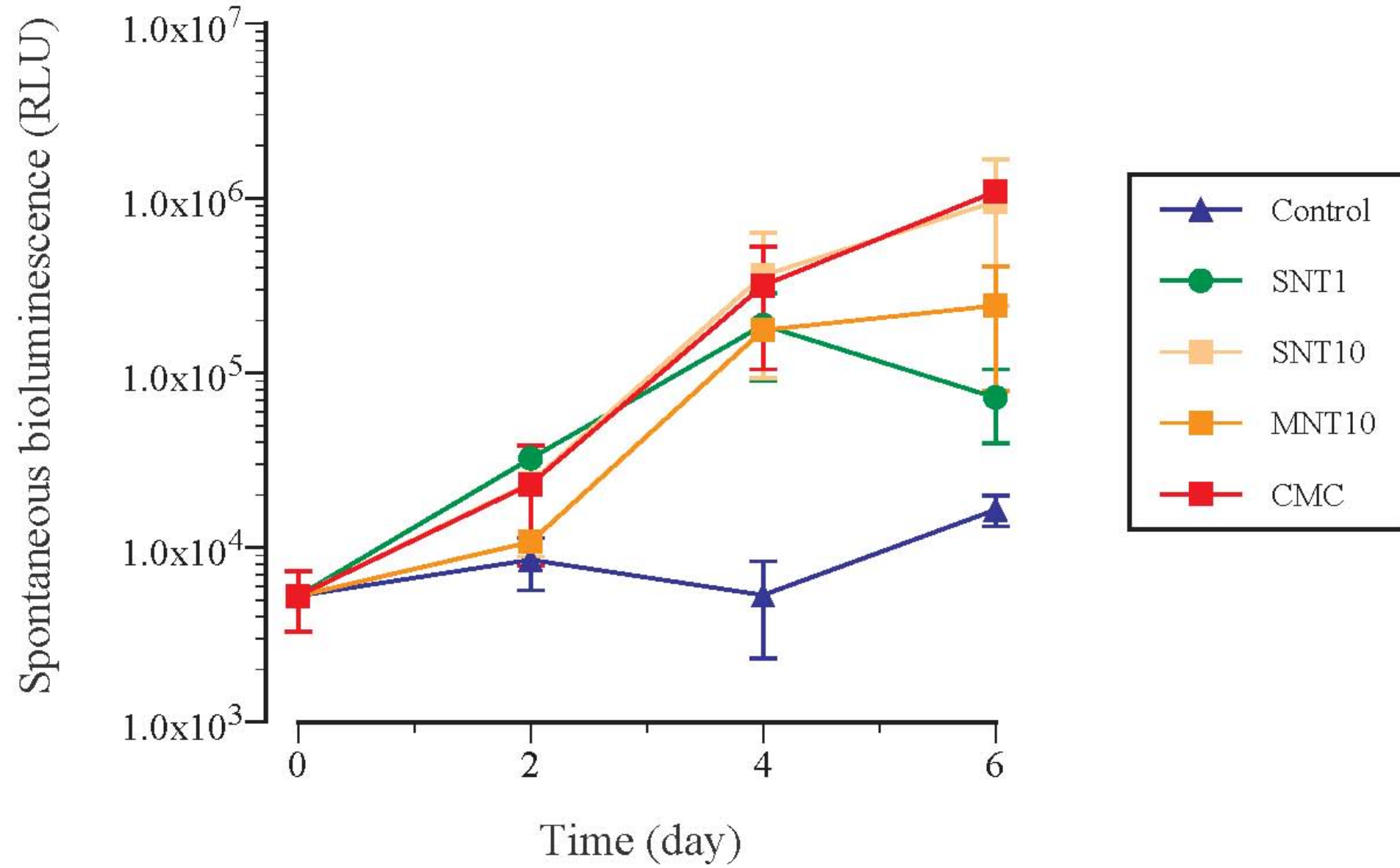
Nanoparticles*	Concentration (ppm)	Abbreviations
Single-Wall Carbon Nanotubes	1 and 10	SNT
Multi-Wall Carbon Nanotubes	10	MNT
<u>Surfactant:</u> Carboxymethyl cellulose	0.1	CMC
Layered Double Hydroxide Colloidal	1 and 10	CLD
Micro Layered Double Hydroxide	10	MLD
<u>Surfactant:</u> Sodium acetate	~10	SA

\* Received from Jeff Gilman group at NIST, National Institute for Standard and Technology

# Time variation of the spontaneous light Nanoparticles



# Time variation of the spontaneous light Nanoparticles

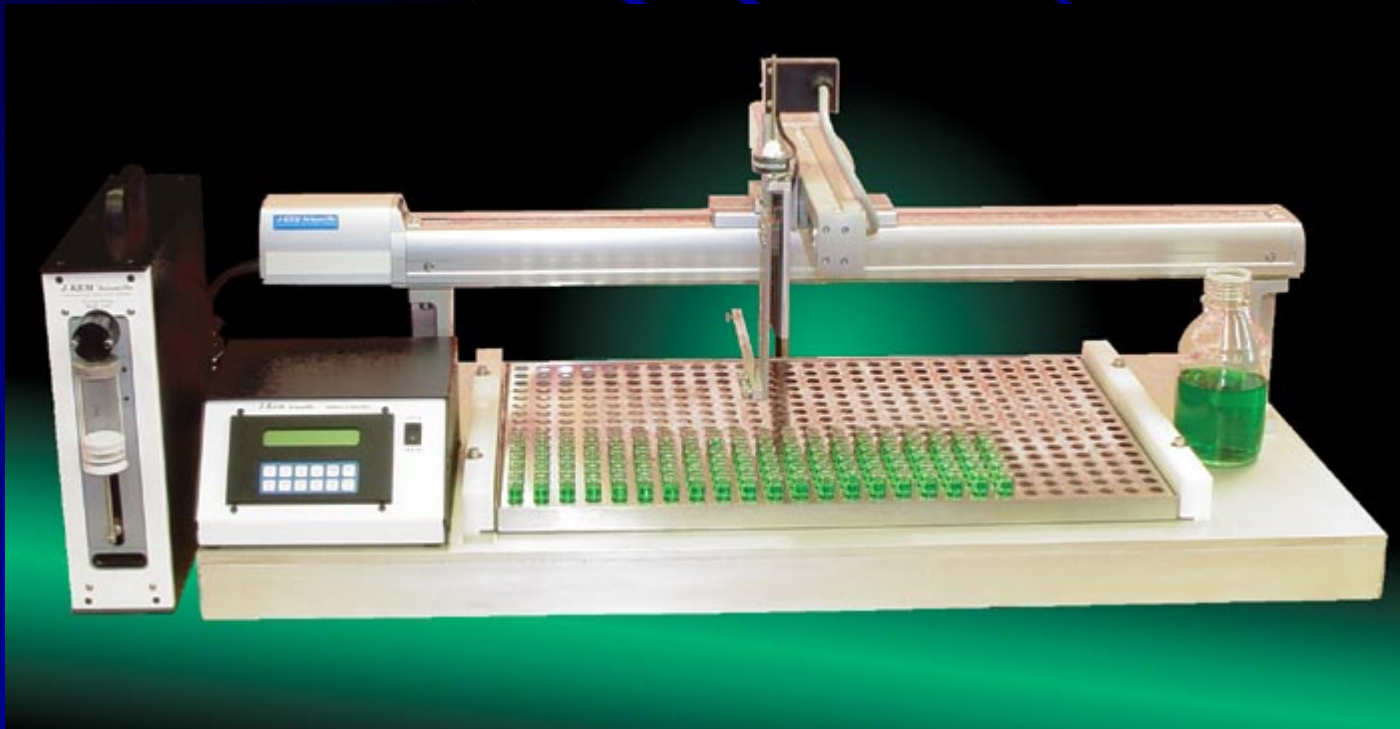


# PARAMETER SPACE FOR POLYMER NANOCOMPOSITES

Polymer	Nano-additive	Organic Treatment	Processing Conditions	Other additives	Flame Retardant
PE	clay	Alkylammonium	Temperature	Stabilizers	Phosphate
PP	POSS	Imidazolium	Shear	Processing	Halogenated
PS	Carbon	Chelates	Residence time	UV	Silicon Based
PA6	Silica	Silated	sonication	Antioxidant	.
PU	LDH	Alkyl	.	Fillers	.
PVC	.	Carboxylate	.	Pigments	.
PC	.	.	.	.	.
PEO	.	.	.	.	.
PMMA	.	.	.	.	.
EVA	.	.	.	.	.
Epoxy	.	.	.	.	.
.	.	.	.	.	.
.	.	.	.	.	.

# Nano-dispersion

- We will use a small-scale automated high throughput liquid handling equipment with the capability of mixing dozens of polyol, nanoadditive combinations to screen for nanoscale mixing with polyols.



# CONCLUSIONS

- An important application of polymer clay nanocomposites is as a flame retardant in polymers.
- flame retardant mechanism of polymer clay nanocomposites appears to be the maintenance of a homogeneous dispersion
- Strathclyde - Clay in Foam passes crib 5 test for UK upholstered furniture
- Carbon Nano Fibers inhibit melt dripping and reduce the flammability
- Grunlan - LBL Coating can be used to remove dripping in foams
- Deheyn/Scripps preliminary data show possible toxic effects from surfactants and nanotubes

# Acknowledgments

**Jeffrey W. Gilman, Richard Harris, Jr., Thomas J. Ohlemiller, Sameer S. Rahatekar, John R. Shields, Takashi Kashiwagi**

Building and Fire Research Laboratory, NIST, Fire Research Division,  
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Marine Biology Research Division,  
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**Roland Krämer**

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**Jaime C. Grunlan**

Department of Mechanical Engineering & Polymer Technology Center (PTC)  
Texas A&M University, College Station, TX

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National Institute of  
Standards and Technology



# THANK YOU



**METHANE ICE  
BURNING**